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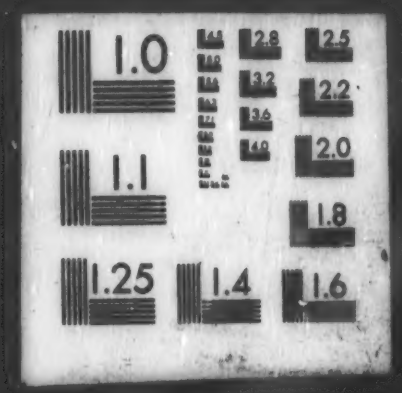

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Followup Study of the Distribution and Fate of Polychlorinated Biphenyls and Benzenes in Soil and Groundwater Samples After an Accidental Spill of Transformer Fluid

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16. Abstracts

A brief discussion of the technical aspects of what happens to spill residuals after cleanup and after a 3 year period. Biodegradation of PCB is looked at, as is the various effects of weather, climate, and soil dynamics.

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Polychlorinated benzenes
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Soil Contamination: PCB
Spills - PCB
Contamination: Soil
PCB
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FOLLOW-UP STUDY

of the

DISTRIBUTION AND FATE OF POLYCHLORINATED BIPHENYLS AND BENZENES

in

SOIL AND GROUND WATER SAMPLES

AFTER AN ACCIDENTAL SPILL OF TRANSFORMER FLUID

-by-

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FOLLOW-UP STUDY OF THE DISTRIBUTION AND FATE OF POLYCHLORINATED BIPHENYLS AND CHLOROBENZENES IN SOIL AND GROUND WATER SAMPLES AFTER AN ACCIDENTAL SPILL OF ASKAREL

BACKGROUND:

On March 5, 1973, an accidental spill of approximately 1500 gallons of askarel occurred in a rural area of East Tennessee. The spill resulted in the environmental contamination of two watersheds because of its location on the crest of a hill. Through the influence of rainfall, geology, and overburden characteristics, the chemical was subsequently dispersed through the soil both horizontally and vertically.

This particular askarel spill was composed of a commercial mixture of polychlorinated biphenyls (Aroclor 1254) and a proprietary solvent of polychlorinated benzenes. Both components were chlorinated hydrocarbons--a class of compounds noted for their persistence in the environment. Consequently, an extensive "clean-up" of the affected area was started on March 14, 1973. To assure the effective removal and proper disposal of the hazardous substances, the contaminated soil was packed and sealed in metal drums before it was taken from the spill site. The removal procedure resulted in extensive excavations in three general areas. After 11,531 drums of contaminated soil were removed, the excavated areas were sealed, backfilled and packed with uncontaminated soil. The entire affected area was subsequently covered with topsoil, seeded with grass, and landscaped.

On March 8, 1973, the Regional Office (Region IV) of the Environmental Protection Agency (EPA) in Atlanta commenced a sampling program of the affected areas to determine the concentration level of contaminants in the soil and water table. Stewart Laboratories, Inc. (SLI), a private laboratory located in Knoxville, Tennessee, joined EPA in the sampling program on March 21, 1973. This sampling program, for monitoring and detection purposes, continued jointly by EPA and SLI for several additional weeks. In addition to the EPA sampling program, Stewart Laboratories provided sampling and analytical assistance during the excavation.

PROJECT OVERVIEW:

The sparsity of knowledge about the fate of PCBs in the environment is illustrated by the recommendation of the Interdepartmental Task Force on PCBs (1) that "more scientific information about PCBs is needed" relative to their occurrence, transfer, and cycling in the environment.

The biologically important characteristics of PCBs are their insolubility in water, high solubility in fats, toxicity to metabolic processes. and extreme chemical stability. The combination of persistence and accumulation in fat during transition through a food chain can result in considerable increases in concentration of the compounds at higher levels in the food chain. Like DDT, PCBs are reported to degrade very slowly under natural conditions (2).

Although laboratory studies (3-7) have suggested pathways in which degradation of Aroclor 1254 in the environment might occur, the actual observation of degradation products in "natural environmentally aged samples" has not been reported to date.

In June 1975 the Environmental Protection Agency awarded a contract to Stewart Laboratories, Inc., for a follow-up study of the distribution and fate of PCBs and polychlorobenzenes two years after the occurrence of the East Tennessee spill.

This project was designed to assist EPA spill response personnel in assessing the degree of soil removal necessary in a PCB land spill situation. Additionally, the sampling of water sources adjacent to the study area was to provide information on the rate of intrusion of lower chlorinated benzenes into ground water.

TECHNICAL APPROACH:

Potential mechanisms for the loss of askarel remaining in the spill site area after the cleanup include volatilization, leaching, metabolic, and nonmetabolic degradation. The experimental approach employed in this study was designed to detect and assess the magnitude of each of these potential routes as loss pathways of the residual askarel from the spill site.

Extensive experimental background data had been obtained by SLI during and after the 1973 clean-up procedures employed at the study site. Correlation of the 1973 data with the results of the 1975 follow-up study would provide a means of assessing the distribution and fate of PCBs and polychlorinated benzenes in a natural environment. Data

obtained by Stewart Laboratories, Inc., during the 1973 site clean-up included: (1) core samples in the bottom of excavation areas immediately prior to fill; (2) core samples at elevations geologically below the spill; (3) water and sediment from a spring well in a watershed below the site; (4) water from domestic wells adjacent and peripheral to the spill area; (5) water from the over-all environment of the general area; and (6) water from a domestic control well.

FIELD COLLECTIONS AND MICROBIOLOGICAL EVALUATIONS:

During the initial phase of the 1975 study, SLI collected 145 cores and 24 water, sediment, and control samples from the immediate spill site environment. Core and control soil samples were examined by established procedures to determine the relative numbers of the major types of microbial flora. Among these were the true bacteria, actinomycetes, and a wide variety of microscopic fungi. The over-all approach in determing microorganism abundance was to isolate those groups which were probable participants in biochemical degradation. In correlation with this, pH, moisture, type of soil, and sample depth influences were researched.

The soil samples, which were various types of clay and chert, were found to have relatively low bacterial, fungal and actinomycete populations. The bacterial population, however, far exceeded populations within the other two groups. Plate counts for these organisms determined in fertile agricultural soil have been shown to be much higher. Average bacterial counts may exceed 15 million

per gram of soil, while smaller fungal and actinomycete populations may average 400 thousand and 700 thousand, respectively (8). Only one of the 142 samples was shown to have a bacterial count as high as three million per gram and only four others exceeded one million per gram of sample. Also, fungal and actinomycete counts in the examined samples were correspondingly lower than those usually found in fertile soils. The two control soil samples, taken from areas remote to the spill, were also surprisingly low for all three types of organisms.

Analysis of microbial populations relative to pH of the soil samples showed that bacterial and actinomycete counts were highest in samples having a pH of 5.0 to 5.9 and lowest in a pH range of 4.0-4.5. Conversely, the number of fungi were highest in the latter range and lowest at a pH of 5.0 or above. It is well recognized that fungi thrive best in a relatively acid environment while bacteria and actinomycetes, in general prefer a more neutral pH range for survival and growth.

Microbial counts were also determined in relation to moisture content of the soil samples. Determinations were made in the ranges of 0-5, 5-10, 10-15, 15-20, 20-25 and 25-30 percent moisture by weight. It was observed that the highest bacterial and actinomycete concentrations were present in samples having 5-10 percent moisture. Fungal counts were the greatest in samples having the least moisture. A single sample having a 25-30 percent moisture was insufficient to provide

valid data at that level. In fertile soils, rich in nutrients, it might be expected that extremely high numbers of organisms would be detected when moisture levels were high, since water is required to solubilize the nutrients, making them most readily available to the soil populations. However, in clay and chert where nutrients are extremely deficient, and where the pH range is predominately between 4.0 and 5.0, soluble acid minerals contributing to the low pH may function bacteriostatically or bactericidally to maintain a low level of organisms. Very significant decreases in bacterial counts were observed when moisture content of the samples exceeded 20 percent, and for actinomycetes when moisture was above 10 percent. Fungal populations decreased steadily as moisture content increased to 20 percent. Above this level, a slight increase in fungi was noted between 20-25 percent moisture. It has been reported (9,10,11) that microbial counts in fertile agricultural soil are the highest in the first 6-8 inches below the surface, decreasing rapidly below that point to only a few hundred per gram at depths of 6 feet or more. Although these data were obtained from samples deficient in nutrients at any depth, a similar trend could be observed. The major difference was revealed by bacterial counts which averaged 157,330 per gram between 0 and 8 inches and increased to 271,700 per gram between 8 and 29 inches. Below 29 inches, the bacterial population was reduced progressively to a total of 2500 per gram in a single sample taken at a depth below 66 inches. Actinomycete counts were highest between 0 and 2 inches and at a depth of 24-29 inches, subsequently decreasing to 100-700 per gram at all depths below 29 inches. Fungal counts were highest between 8 and 27 inches, and these also decreased progressively below

that level except for a very slight increase in numbers in 13 samples taken at a depth between 56 and 61 inches.

The fact that bacterial counts near the surface of the soil were slightly lower than at depths of 8-29 inches, may possibly be attributed to the seasonal effect of high summer temperatures which would tend to kill some of the organisms by baking of the soil to shallow depths.

Analysis of microbial populations exposed to polychlorinated biphenyl (PCB) in the soil suggested a possible stimulating effect of this compound in concentrations between 0.05 and 5.0 mg/Kg on both the bacteria and actinomycetes. The lowest bacterial counts were obtained in samples where PCB levels were less than 0.05 mg/Kg. Although only three samples were contanimated with PCB in excess of 10 mg/Kg, the bacterial counts were greater than in relatively uncontaminated soil having less than 0.05 mg/Kg. Fungal counts were essentially unaffected in most cases.

In summary, the relatively low microbial counts are compatible with the clay and chert soils which are largely devoid of nutrients. The soil acidity is also reflected by the low bacterial counts. Excessive moisture did not appear to influence an increase in the microbial populations of the soil, and in fact, the lowest bacterial and actinomycete counts were observed in samples having a moisture content of 20-25 percent while the highest numbers were found in samples having 0.5-10.0 percent moisture.

The most interesting observation was the apparent stimulating effect of 0.05-5.0 mg/kg of the polychlorinated biphenyl compounds. Bacterial counts in 55 samples were shown to be 50 percent higher than the mean for all 142 samples and actinomycete counts were similarly 100 percent greater.

ANALYTICAL METHODOLOGY AND EVALUATIONS:

The second phase of the study provided the analytical data necessary to evaluate any changes which might have occurred over the past two years. Identical analysis procedures were employed for the determination of PCB content in both the present study and the 1973 project. Careful choices were made as to which samples should be confirmed by quality assurance checks and identified by GC/MS analysis. All outside quality assurance and requested isomer identifications were done by The Surveillance and Analysis Division, Region IV, EPA, in Athens, Georgia.

Aliquots from all of the soil and water samples collected from the spill area were analyzed quantitatively for Aroclor 1254 by electron-capture gas chromatography (GC/EC). PCBs were detected in 68 of the 147 core samples. Concentrations ranged from 0.05 to 67 mg/Kg on a dry basis. The nineteen water samples included in this study were analyzed for Aroclor 1254 and the askarel solvent by EC/GC. No PCBs were detected in any of the water samples at the 0.5 ppb level. Solvent, at the 1. ppb level, was detected in two of the 19 samples.

Gas chromatography-mass spectrometry (GC/MS) was used to compare the homolog distribution of PCBs in selected 1975 samples to the distribution exhibited in a sample of askarel from the 1973 spill. Verification of the presence or absence of degradation products was also performed by this technique.

STUDY CONCLUSIONS:

Distribution of Aroclor 1254.

In order to effectively evaluate the 1975 distribution of Aroclor 1254, pertinent facts relative to the spill itself need to be considered. The magnitude of the 1973 spill and the elevation contours of the semi-mountainous terrain of the spill site assured an initial mass flow transport process, which resulted in complete saturation of the topsoil, with varying degrees of penetration into the clay overburden over a relatively large area in both horizontal and vertical directions. The spread of the askarel was also affected by the movement of contaminated surface water resulting from massive rainfall in the weeks immediately following the spill.

Excavation operations revealed that the distribution in the clay was non-uniform, and numerous so-called "hot spots" resulted from movement along the root systems of plants and trees as well as from movement in the fractured chert frequently found in the clay matrix.

One stated purpose of the study was to determine if a reduction in concentration of Aroclor 1254 in the soil had occurred either as a

result of migration from the spill area or from degradation. By direct comparison, the 1973 data are higher in 61% of the locations; but the order of magnitude for the Aroclor 1254 concentrations are comparable for both years; and no significant migration patterns are observed.

Another means of measuring soil migration is to observe surface-to-ground water flow through the mechanism of leaching. The 1973 data showed only minimal movement of Aroclor 1254 in the ground water. Only two ground water sampling stations gave positive data for Aroclor 1254. These locations were a spring just below the spill area and a well less than one hundred feet from the spill excavation area. The highest Aroclor 1254 concentration ever detected in a water sample in 1973 was 2.1 ppb. These two sampling stations were among the eight wells, one spring, and one creek which were sampled in the 1975 follow-up study. No PCBs were detected in any of these samples at the 0.5 ppb level.

Based on a comparison of the 1973 and 1975 concentration profiles for both cores and water, it is evident that no significant reduction in the concentration of Aroclor 1254 in the soil has occurred as the result of migration.

Degradation of Aroclor 1254.

Two possible degradation modes exist--metabolic and nonmetabolic. Each degradation mechanism will now be considered from the standpoint of applicability to the system under study.

1. Chemical Transformation--The non-biological alteration of a chemical introduced into any part of the environment is dependent on the moisture, pH, and temperature of that environment, on the nature of reactive groups on the agent and on the presence of catalytic sites. In addition, the nature and intensity of available illumination determines photochemical reactions.

   Irradiation (photolysis) of Aroclor 1254 under laboratory conditions has produced dechlorinated products; and, in the presence of air and water, hydroxylated and hydrated products have been identified in the polar products of the irradiation. Although these theoretical routes for chemical degradation exist, the extreme stability (chemical inertness) of Aroclor 1254 coupled with the absence of illumination at the potential reaction site make chemical transformation a highly improbable degradation mechanism.

2. Biological Alteration--Biological alteration is assumed to be catalyzed by enzymes. Biochemical alteration of environmental contaminants and agents can be viewed as a function of the expression of genetic material in coordination with the ability of the environment and the biological species to provide for synthesis of enzyme and cofactors to support the reaction. Changes in the course of this expression may be one of the biological effects interacting strongly on the disposition of a particular chemical. By analogy with the dechlorination of

DDT to DDD by soil microorganisms, biodegradation of Aroclor 1254 is considered to be a possible degradation mechanism in a natural environment.

3. Aroclor 1254 Degradation Assessment--Aroclor 1254 is a mixture of chlorinated biphenyl homologs. If there were no degradation in the environment, or if all homologs degraded at the same rate, the ratio of homologs in "aged environmental samples" should be the same as that in the askarel introduced into the environment at the time of the spill. On the other hand, if the homolog ratio in the samples from the spill site differs from that of the askarel spilled, some process(es) must be operating in the environment to remove different homologs at different rates. According to data supplied by the Monsanto Company,[12] the typical percent (w/w) composition of Aroclor 1254 is similar to that given in Table 1.

TABLE 1. Typical Homolog Composition of Aroclor 1254

Homolog (No. of Chlorine/biphenyl)	Aroclor 1254*
0	<0.1
1	<0.1
2	<0.5
3	1.
4	21.
5	48.
6	23.
7	6.
8	ND†

*Percent (w/w) by GC/Mass using area correlation factors by homolog response.
†ND = None Detected, <0.01%.

All chromatograms from the EC/GC analyses of 1975 samples were carefully examined for peak alterations and for the appearance of new peaks with reference to the chromatogram of the askarel released into the environment at the time of the spill. Comparative chromatograms for Aroclor 1254 in a typical "aged environmental sample" and Aroclor 1254 in the askarel spilled in 1973 revealed that the ratio of homologs in the environmental sample is the same as that in the askarel introduced into the environment at the time of the spill. These results indicate that either there has been no degradation in the environment or that all homologs have degraded at the same rate.

Using gas chromatography-mass spectrometry (GC/MS), the homolog distribution of selected 1975 samples was compared to the distribution exhibited in a sample of askarel from the 1973 spill. These data also confirm that the ratio of homologs in the environmental samples is the same as that of the askarel spilled in 1973.

No evidence was found by GC/MS and/or EC/GC to indicate the presence of degradation products in any of the "aged environmental samples" collected in or around the spill site. Primary biodegradation can be defined as minimum alteration of the chemical structure of the material in question to an extent that characteristic properties of the original material are no longer evident.

Based on the experimental evidence collected and considering the definition just presented, it may be concluded that no detectable reduction in the concentration of Aroclor 1254 in the soil has occurred as the result of chemical transformation or biodegradation. This conclusion is consistent with the distribution profile of the occurrence of major soil microorganisms as derived from the microbiological evaluation of the spill site.

Askarel Solvent Intrusion Into Ground Water.

Another goal of this study was to determine the rate of intrusion of polychlorobenzenes into ground water. Migration of the askarel solvent was completely different from that observed for the PCBs, Aroclor 1254.

Differential migration of the askarel solvent in the spill environment was observed by SLI analysts in a well water sample collected March 22, 1973. A subsequent screening of selected water sources--wells, creeks, ponds, etc.--revealed an interesting phenomenon. There were two distinct patterns for the solvent concentration in the water samples. One closely resembled the component distribution of the askarel solvent spilled. The other was almost 95% trichlorobenzene.

Because of this observed phenomenon, a selected number of representative core drillings at the spill site were analyzed for askarel solvent. These data indicated that tetra- and penta-chlorobenzene were preferentially retained in the soil while the other solvent components--

especially the trichlorobenzenes had selectively moved out of the area. This study also showed that Aroclor 1254 was preferentially retained in the soil. Data from monitoring programs confirmed that water samples with solvent patterns resembling the askarel solvent component distribution indicated possible contamination by surface water run-off and seepage of surface water into a supply. Water with the high trichlorobenzene concentrations indicated intrusion of these solvent components into the ground water supply. Solvent concentration in the well located closest to the spill site reached a maximum of more than 500 ppb on April 7, 1973. However, by the time the spill site excavations were completed, the level had dropped to less than 25 ppb. Samples from this station collected during the 1975 follow-up study still show solvent present in the water at the 1.0 ppb concentration level.

These data clearly indicate that the more water soluble components of the askarel solvent invaded the ground water supply almost immediately after the occurrence of the spill. Leaching was the migration mechanism responsible for the intrusion of the lower chlorinated benzenes into the ground water supply.

Based on the 1973 and 1975 data, it can be concluded that intrusion of lower chlorinated benzenes into a ground water supply occurred rapidly after the spill. This same water supply contains minimal but detectable quantities of askarel solvent two years after the occurrence of the spill.

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